

Dispersion of CaCO_3 nanoparticles by sonication and surfactant treatment for application in fly ash–cement systems

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Abstract This research aims to offset the negative effects of fly ash on the early-age properties of cementitious materials with the use of calcium carbonate (CaCO_3) nanoparticles. The main focus is to enhance the effect of the nanoparticles by improving dispersion through ultrasonication and use of surfactants. CaCO_3 aqueous suspensions with various surfactant types and concentrations are prepared and subjected to different sonication protocols (varying duration and amplitude). Dispersion and stability are quantitatively measured by comparing their absorbance spectra through spectrophotometry and qualitatively evaluated through SEM imaging. The effectiveness of sonicated CaCO_3 nanoparticle additions in accelerating setting and improving early-age compressive strength gain of fly ash–cement pastes is investigated. The sonication protocol is optimized and

the most effective dispersion is achieved with polycarboxylate-based superplasticizer. Good agreement is found between the dispersion measurements and mechanical performance.

Keywords Calcium carbonate · Nanoparticles · Dispersion · Sonication · Fly ash · Cement and Concrete

1 Introduction

With increasing societal demands to make concrete a more sustainable infrastructural material, the replacement of cement with supplementary cementitious materials (SCMs) has been widely recognized as a viable solution. One such SCM is fly ash, a coal combustion byproduct that can introduce advantages to the rheological and long-term properties of concrete. However, it is known to negatively impact the early-age properties. Due to the pozzolanic nature of fly ash, a secondary reaction that can only occur after primary cement hydration, it significantly slows setting and early-age compressive strength gain, both of which slow construction. To further promote the use of fly ash, there is a need to offset these negative effects.

The use of nanoparticles has been demonstrated to activate cement hydration, which can help to accelerate the formation of calcium hydroxide (CH) and

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subsequently initiate the pozzolanic activity of fly ash. Thus far, most studies have focused on nanosilica and demonstrated its effectiveness in improving the early-age properties [26, 39, 45]. However, a recent study by Hou et al. [23] showed that it may have negative effects on the later-age properties. Also being a pozzolan, nanosilica is in direct competition with fly ash for CH. Furthermore, due to the fineness of nanosilica, it exhibits higher reactivity, which results in high rate of CH consumption at early ages. Although this has good implications on the early-age properties, it leaves less CH for fly ash to react with later on to sustain long-term strength gain. As the suitability of nanosilica for fly ash–cement systems remains inconclusive, it is necessary to look for alternative types of nanoparticles for the application of activating fly ash–cement systems.

Limestone, or calcium carbonate (CaCO_3), is primarily used as a filler to improve rheological properties in its powder form; however it has also been shown to affect cement hydration. Studies have shown that CaCO_3 can accelerate early-age hydration, provide nucleation sites for C–S–H (and perhaps CH), and react with calcium aluminates (C_3A) and tricalcium silicate (C_3S) to produce calcium carboaluminates and calcium carboasilicate hydrates, respectively [5, 7, 15, 22, 24, 29, 30, 34, 42, 54]. Given these effects, CaCO_3 is considered to be a good candidate for inclusion in fly ash–cement systems. Thus far the focus has mainly been on micro-sized limestone powder. Nano CaCO_3 has not been as widely investigated but studies have shown the potential of the material in offsetting the negative effects of fly ash on the early-age properties, even at high replacement rates [5, 8, 20, 36, 47, 48].

From a practical standpoint, the effective use of nanoparticles relies on the ability to achieve uniform and stable dispersions. This is expected to enhance their performance and reduce the necessary amount of materials for applications, which ensures its economic viability. One of the major challenges in using nanoparticles over microparticles is that uniform dispersion becomes significantly more challenging. Due to their high surface area and energy, nanoparticles experience increased surface interactions and are more susceptible to particle adhesion upon direct contact by van der Waals, electrostatic and magnetic forces. Although a critical issue, dispersion is not addressed in most studies regarding nanoparticles in cement and concrete research, as reported in a paper by

Bagheri et al. [4]. In this study, we explore methods to obtain well-dispersed, stable CaCO_3 nanoparticles in an aqueous medium through sonication and the use of surfactants. Previous work by the authors has demonstrated the potential of the method [28]. Various sonication protocols and surfactant types are investigated. Dispersion quality and stability are quantitatively measured through methods that utilize optical absorbance spectroscopy. They are also qualitatively confirmed through SEM imaging. Degree of dispersion is then tied to the influence of the nanoparticles on the early-age properties of fly ash–cement pastes (CPs).

2 Materials and experimental methods

2.1 Materials

Type I Portland cement and tap water are used in all samples. Type F fly ash is used in select mixes. The chemical composition of the cement and fly ash are shown in Table 1. The CaCO_3 nanoparticles (from Reade Advanced Materials) are in dry powder form and have a particle size range of 15–40 nm according to the manufacturer. From the SEM image, shown in Fig. 1, it is apparent that the as-received material consists of aggregates on the micron scale.

A number of surfactants are tested to determine their suitability to disperse and stabilize the CaCO_3 nanoparticles in aqueous solution. They are listed in Table 2 and their chemical structures are shown in Fig. 2. Two commercially based superplasticizers are tested: one naphthalene-based (WR Grace) and one polycarboxylate based (BASF). Two anionic,

Table 1 Chemical composition of cement and fly ash

| Materials | Type I cement | Type F fly ash |
|-------------------------|---------------|----------------|
| SiO_2 | 20.2 | 46 |
| Al_2O_3 | 4.7 | 17.8 |
| Fe_2O_3 | 3.3 | 18.2 |
| SO_3 | 3.3 | 2.59 |
| CaO | 62.9 | 8.4 |
| MgO | 2.7 | 0.95 |
| Na_2O | / | 0.59 |
| K_2O | / | 2.16 |
| LOI | 1.1 | 1.49 |
| Total | 98.2 | 98.2 |

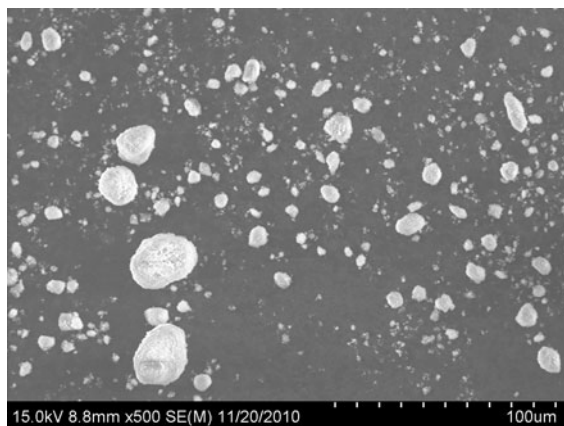


Fig. 1 SEM image of aggregated CaCO_3 nanoparticles in the dry powder form [27]

amphiphilic surfactants are tested: sodium cholate (SC) (Sigma Aldrich) and sodium dodecyl sulfate (SDS) (Fisher Scientific), respectively. And three variants of a nonionic, amphiphilic block copolymer with polypropylene oxide and polyethylene oxide chains (T1109, T904, T908) are tested, from BASF. Cationic surfactants are not tested, as they have been found to flocculate CaCO_3 [25, 38, 41]. SC and SDS are chosen here as they have been widely used as surfactants for carbon-based nanomaterials, where they demonstrate exceptional dispersion stability and ability to isolate a variety of low-dimensional structures including nanotubes and nanosheets [2, 17, 18, 50]. The Tetronic block copolymers are also popular dispersants for such carbon systems [1, 49] and will be studied to explore their suitability with non-carbon nanoparticles as surfactants. Tetronics block copolymers follow a naming convention where the last digit of their name multiplied by 10 indicates the percentage by weight of their hydrophilic chains, while the

earlier digits multiplied by 45 provide the approximate molecular weight of the hydroblock segment.

2.2 Experimental methods

2.2.1 Dispersion in aqueous solution

2.2.1.1 Horn sonication To break up the aggregated CaCO_3 nanoparticles in aqueous solution, ultrasonication (Fisher Scientific model 500 Sonic Dismembrator) is implemented. Each constituent (i.e. nano CaCO_3 , water, and surfactant) is measured directly into a metal cup using a precision scale. Then, the sample is placed in the holder and lifted up so the tip of the horn is submerged in the solution but not touching the base of the metal cup. An ice bath is placed on a holder, as well, and raised up to surround the sample to prevent overheating and evaporation during the sonication process. The sonic dismembrator is programmed to apply a constant sonication for a set duration and amplitude.

2.2.1.2 Bath sonication The maximum capacity for horn sonication (HS) is approximately 200 mL. In order to utilize these suspensions for preparing paste samples for mechanical testing, they are scaled up by bath sonication (Bransonic 3510 tabletop ultrasonic cleaner). The bath sonicator used in this study allows for up to 2 L of solution to be prepared. The samples are placed in a holder within the bath to prevent direct contact with the walls of the sonicator. Sonication is performed at room temperature. The water is degassed for 10 min prior to sonication and the initial water level is kept consistent for all samples.

2.2.2 Evaluating dispersion

To obtain a quantitative measure of dispersion, the absorbance spectra of nano CaCO_3 aqueous suspensions are measured by a spectrophotometer (Varian Cary 5000). According to Beer's law, the optical absorbance of solution-phase suspension exhibits a linear relationship with the concentration of substance. It is expected that nanoparticles that are dispersed and stabilized will remain in suspension. On the other hand, any aggregated particles will settle to the bottom. By noting the decrease in optical density of samples, it is possible to deduce the extent of sedimentation and thus the quality of dispersions prepared via various sonication protocols and surfactants.

Table 2 List of surfactants

| Surfactant | Type |
|------------|---|
| N | Naphthalene-based superplasticizer |
| PC | Polycarboxylate-based superplasticizer |
| SC | Sodium cholate |
| SDS | Sodium dodecyl sulfate |
| T1109 | Variants of a nonionic, amphiphilic block copolymers with polypropylene oxide and polyethylene oxide chains |
| T904 | |
| T908 | |
| | |

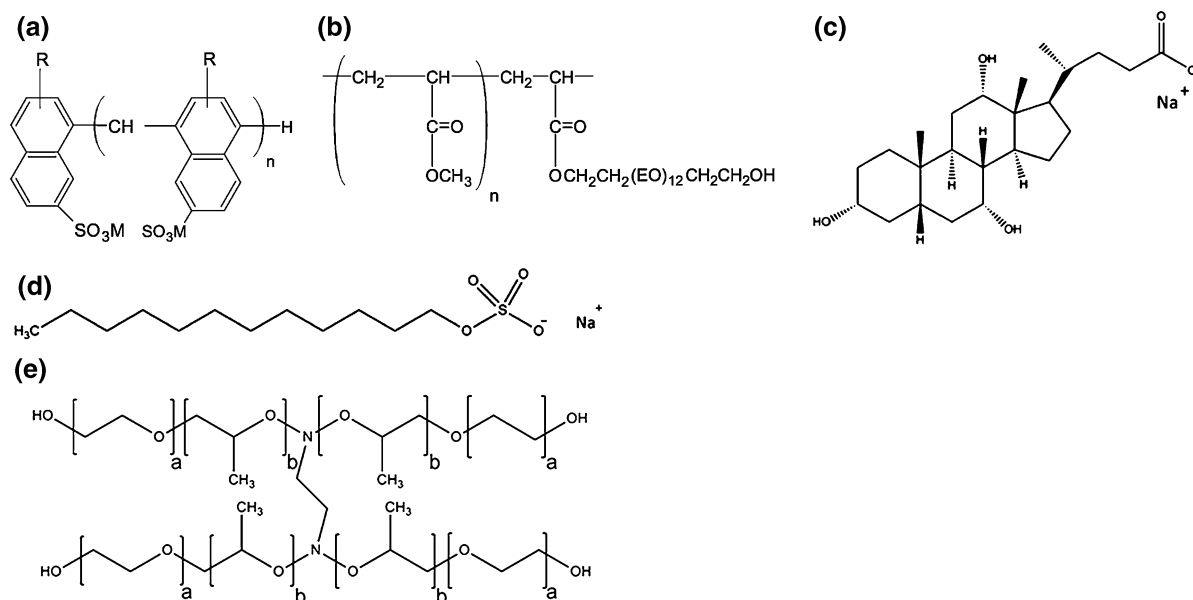


Fig. 2 Chemical structures of surfactants: **a** naphthalene-based superplasticizer and **b** polycarboxylate-based superplasticizer [35]; **c** SC, **d** SDS, and **e** Tetriconic

In order to ensure that the spectra measured are only of the suspended nanoparticles and not the surfactant, baseline readings are taken before each set of measurements. All spectra readings are taken between wavelengths of 380–800 nm and the absorbance at 550 nm is compared. Tested suspensions are diluted with surfactant solution to prevent over-saturation of the absorbance from samples with nanoparticles: 50 μ L of CaCO₃ suspension is placed in a cuvette and then diluted with 800 μ L of surfactant solution. Before each reading, the cuvettes are agitated using a vortex mixer/shaker to obtain a uniform sample. In all cases, three samples are measured and the average is taken to be the representative absorbance. Detailed information on the procedures for all test methods can be found elsewhere [27].

2.2.2.1 Centrifugal method The absorbance spectra are measured for the supernatant of centrifuged nanoCaCO₃ suspensions and suspensions obtained immediately after sonication. The latter serves as a reference point, at which the majority of nanoparticles are expected to be suspended momentarily. During centrifugation any undispersed, aggregated particles will sediment to the bottom while the dispersed nanoparticles will remain suspended in the supernatant. By comparing the absorbance before and after centrifugation, a measure of degree of dispersion after sonication is obtained.

Suspensions are transferred to conical micro-centrifuge tubes, then centrifuged at 5,000 rpm for 2 min. After centrifugation, 50 μ L of the supernatant is decanted, placed in a cuvette and diluted with 800 μ L of surfactant solution. Similar steps are followed for the reference samples obtained immediately after sonication.

2.2.2.2 Sedimentation over time The centrifugation method subjects the suspensions to high centripetal force over a short period of time. Although this provides a quick measure of degree of dispersion, it is of interest to measure the sedimentation of nanoparticles over time when the suspension is left at rest. During sonication the nanoparticles may be broken up into primary particles or primary aggregates but it is possible that they will reaggregate over time. To measure the rate at which this is occurring, the evolution of sedimentation is measured.

The change in absorbance of the suspension is monitored up to 24 h. Immediately after sonication, 15 micro-centrifuge tubes are each filled with 1.5 mL of the suspension with a Pasteur pipette. Then at 0, 0.5, 3, 6 and 24 h, 1.0 mL of supernatant from three samples are decanted and transferred to three new centrifuge tubes. Cuvettes are filled with 50 μ L of the decanted solution and 800 μ L of surfactant solution, then tested. Monitoring the decrease in absorbance over time gives

a measure of the rate of reaggregation when the suspension is left at rest.

2.2.3 Early-age properties

The setting and compressive strength gain of CPs with a 30 % fly ash replacement by mass and a w/b ratio of 0.35 are measured. Pastes are prepared in a small upright mixer for 10 min at the lowest setting. When nanoCaCO₃ is added, it is introduced as an aqueous suspension and the water content of the suspension serves as the mixing water for the sample. This suspension is added to the dry ingredients, i.e. cement and fly ash, during mixing.

Setting time of pastes are measured using the Vicat needle test based on ASTM standard C191-08. And compressive strength of cubic samples [50 mm] at 1, 3, and 7 are measured in accordance to ASTM standard C109/C109 M-08. 3 and 7 days samples are cured in water at room temperature until testing. Three samples are tested for each mix, from which the average is taken to be the representative measurement.

2.2.4 Scanning electron microscopy (SEM)

Hitachi S-4800 FE-SEM equipped with energy dispersive spectroscopy (EDS) is used to characterize the state of dispersion of the CaCO₃ nanoparticles. For nanoCaCO₃ aqueous suspensions, a drop is placed on a sample holder and allowed to dry under ambient conditions for at least 2 h. For hardened CP samples, a fractured piece obtained after compressive strength testing is soaked in acetone to stop hydration. All samples are coated with 20–25 nm of gold. The accelerating voltage and current are 15–20 kV and 10–20 μ A, respectively. The SEM is set so that the upper detector collects the secondary electrons.

3 Experimental results and discussion

3.1 Dispersion in aqueous solution

3.1.1 Centrifugal method

3.1.1.1 Influence of surfactant type To determine the effect of surfactant type, all suspensions are subjected to the same sonication protocol: HS for 3 h at 40 % amplitude, the total energy of which is

356,400 J. The results are shown in Table 3. Sedimentation is defined as the following:

$$S = 100 \% - \frac{\text{Abs}_C}{\text{Abs}_{t=0}} \cdot 100 \% \quad (1)$$

where $\text{Abs}_{t=0}$ is absorbance at 550 nm for the suspension immediately after sonication (reading taken within 5 min after end of sonication) and Abs_C is absorbance at 550 nm of the supernatant after centrifugation. In the case of no surfactant, all of the nanoparticles settle to the bottom. It is apparent that although CaCO₃ is considered to be hydrophilic, the degree of hydrophilicity is not high enough to prevent the large particles from reaggregating. Therefore, this proves that the use of surfactants is necessary for stabilization.

A range of dosages for each surfactant is tested (7–200 % surfactant by mass of nanoCaCO₃) but only select results, which are considered to be representative, are included herein. It is apparent from Table 3 that among the surfactants presented in this study, PC showed the highest effectiveness where almost 10 % of the CaCO₃ nanoparticles are retained after centrifugation. SC and SDS are considered to be conventional anionic surfactants that exhibit amphiphilic properties, where SC has a planar structure while SDS is linearly shaped. Adsorption of the surfactant onto the CaCO₃ is expected to occur by both electrostatic interaction with the Ca²⁺ sites and hydrophobic bonding. Although anionic surfactants have been found to disperse micro-sized limestone particles [40, 46], it is found here that they are not sufficient

Table 3 Influence of surfactant type on dispersion: all suspensions contain 3 g CaCO₃ nanoparticles and 129 g of water [27]

| Surfactant type | Surfactant (g) | Sedimentation (%) |
|-----------------|----------------|-------------------|
| None | 0 | – |
| N | 1 | 97.7 |
| PC | 1 | 92.1 |
| SC | 1.3 | – |
| SDS | 1.3 | – |
| T1109 | 3 | – |
| T904 | 3 | – |
| T908 | 3 | – |

Sedimentation marked with a “–” indicate supernatants which run clear after centrifugation, i.e. all the nanoparticles in the suspension settle to the bottom

in the case of nano-sized particles, where suspensions remained clearly segregated.

Results indicate that PC is the most effective. Although the exact formulation is not known, generally PC superplasticizers are comb polymers consisting of an anionic backbone with carboxylic acid groups and grafted side chains mainly composed of hydrophilic polyethylene oxide (PEO) units. The improvement in nanoCaCO₃ dispersion by PC may be attributed to both electrostatic and steric hindrance: the anionic backbone adsorbs onto the calcium and the PEO chains extend out between adjacent nanoparticles. Polyacrylates, or acrylic acids (sodium [3, 14] and ammonium [19]), have been found to be effective dispersants for CaCO₃ powders, including nanoparticles [11], as they readily adsorb onto their surface. Acrylic acids are a type of carboxylic acid. Therefore the carboxylate (an ether of carboxylic acid) backbone of the superplasticizer should be adsorbing onto the nanoCaCO₃ in a similar manner.

The naphthalene-based superplasticizer did not yield good dispersions. While PCs disperse through electrostatic and steric repulsion with the anionic backbone and PEO chains, respectively, naphthalene-based superplasticizers act only through electrostatic repulsion [6, 9, 10]. Similarly to the SC and SDS, this is not sufficient for dispersing the CaCO₃ nanoparticles in an aqueous solution.

Three variants of a non-ionic, amphiphilic block copolymer are studied. They are commercially available poloxamine: X-shaped and formed by four polypropylene oxide (PPO)–PEO chains bonded to an ethylene diamine central group, where the molecular weight of the PPO and PEO chains can be changed. Seo et al. [49] found that the molecular weight of each of the chains had a significant influence on the dispersability of graphene in aqueous solution. None of the variants, however, are effective in dispersing the nanoCaCO₃. This is likely due to the difference in surface properties between graphene and CaCO₃.

3.1.1.2 Influence of sonication amplitude and duration To verify that sonication is aiding the dispersion process, the absorbance of the suspension treated with PC and prepared by mechanical stirring is evaluated. Dispersion is compared for suspensions that are sonicated for 3 h at 40 % amplitude and mechanically stirred for 3 h. Both suspensions are

treated with PC at a concentration of 33 % by mass of nanoCaCO₃. It is found that the sedimentation of the mechanically stirred suspension is 99.1 %, compared to 92.1 % for the sonicated. This verifies that sonication is enhancing the dispersion process by physically breaking up the aggregates while PC is acting to stabilize the nanoparticles once they are dispersed.

The level of dispersion for suspensions treated with 33 % PC by mass of nanoCaCO₃ subjected to ultrasonication for different durations and amplitudes are presented in Table 4. This is to determine the protocol that achieves the best dispersion while limiting the amount of energy required for processing the nanoparticles. Evaluating the influence of duration, the sedimentation between 1, 3, and 6 h at a fixed amplitude of 40 % are compared. It is found that dispersion improves with duration. However, the rate of decrease in sedimentation goes down—the decrease from 1 to 3 h is greater than that from 3 to 6 h.

To determine the effect of amplitude, samples treated with amplitudes of 35, 40, and 50 % for a fixed duration of 3 h are compared. Decreasing the amplitude from 40 to 35 % results in a notable increase in sedimentation from 92.1 to 98.9 %. On the other hand, an increase from 40 to 50 % does not result in any apparent improvement. There appears to be a threshold for amplitude—beyond 40 % there is no significant improvement in dispersion for the given sonication setup. Regarding duration, although longer duration shows an improvement in level of dispersion, the energy demand increases disproportionately to it. It is likely that the sedimentation is tied to issues of reaggregation, as observed in another study where the aggregate size of sonicated nanoparticles increased from 500 nm to 3–4 µm [37].

Table 4 Influence of time and amplitude of sonication on dispersion: all suspensions contain 1 g PC, 3 g CaCO₃ nanoparticles, and 129 g water [27]

| Time (h) | Amplitude (%) | Energy (J) | Sedimentation (%) |
|----------|---------------|------------|-------------------|
| 1 | 40 | 118,800 | 95.1 |
| 3 | 40 | 356,400 | 92.1 |
| 6 | 40 | 712,800 | 90.2 |
| 3 | 50 | 475,200 | 92.9 |
| 3 | 35 | 311,850 | 98.9 |
| 6 | 30 | 534,600 | 96.5 |

There have been some reported cases where high energy input induced reaggregation [32]. In order to verify this, in the present study a sample is prepared by applying lower amplitude for a longer duration (6 h at 30 %). However this is not found to improve dispersion. The results suggest that instead of improving dispersion through modifying the sonication protocol, which will affect the size of aggregates but not necessarily prevent reaggregation, it is more efficient to find a more suitable surfactant that will stabilize the particles once they are dispersed.

3.1.1.3 Influence of concentration The influence of surfactant concentration is determined. Based on the previously discussed results, samples are treated with PC and sonicated for 3 h at 40 %. NanoCaCO₃ suspensions treated with different concentrations are tested and the results are shown in Table 5. Sedimentation of suspensions treated with 17 and 33 % PC are comparable, whereas at 7 % it increases substantially.

3.1.2 Sedimentation over time

The sedimentation over time at rest of PC treated nanoparticles is measured. The evolution of sedimentation is recorded for suspensions prepared by horn and bath sonication. All suspensions are treated with PC at a concentration of 33 % by mass of nanoCaCO₃. For the suspension prepared by HS, it is subjected to sonication for 3 h at 40 % amplitude. Bath sonication is a much less energy intensive method and thereby requires a longer duration. Suspensions prepared by bath sonication for 6 and 9 h (BS6 and BS9) are compared. The absorbance from 380 to 800 nm of each sample immediately after sonication is shown in Fig. 3 considered as the initial reading. As shown, the optical density of each sample is similar, indicating that the initial degree of dispersion achieved is comparable between all the suspensions. The

absorbance at 550 nm is normalized and plotted as amount retained in Fig. 4. The sample that is horn sonicated exhibits a lower sedimentation rate compared to both bath sonicated samples. Over the first 30 min, retention drops 10 % for BS6 and BS9 while it drops less than 5 % for HS. After 30 min, the rate of sedimentation is about the same between all the samples up to 3 h. At 24 h, BS6 is found to experience the highest sedimentation.

Although PCs are found to be the best dispersant in the present study, the percent retained is still relatively low: approximately 10 % as measured by the centrifugal method and 60 % at 24 h by the sedimentation method. Although PC is expected to adsorb onto

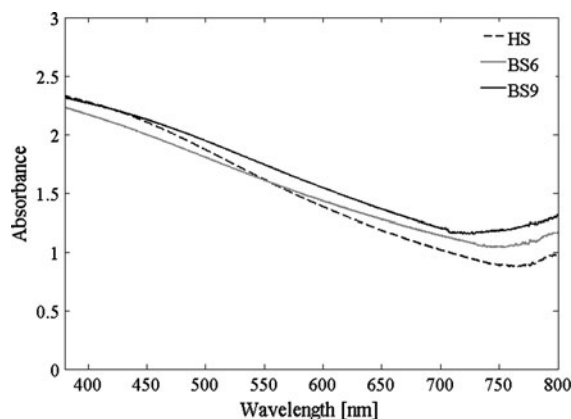


Fig. 3 Absorbance spectra of suspensions immediately after sonication: horn sonicated (HS), bath sonicated for 6 h (BS6) and 9 h (BS9) [27]

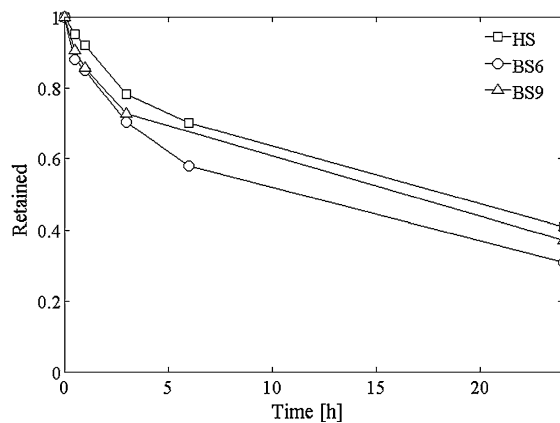


Fig. 4 NanoCaCO₃ retained in suspension (normalized) over time: horn sonicated (HS), bath sonicated for 6 h (BS6) and 9 h (BS9) [27]

Table 5 Influence of PC addition on dispersion: all suspensions horn sonicated for 3 h at 40 % amplitude [27]

| PC (% by mass of nanoCaCO ₃) | Sedimentation (%) |
|--|-------------------|
| 7 | 99.9 |
| 17 | 92.3 |
| 33 | 92.1 |

calcium, the fine size of the nanoparticles may be a critical factor. The high surface area significantly increases adsorption demand and uneven adsorption will lead to aggregation. Further, there are cases where poor adsorption of PC-based superplasticizers on calcite has been reported [12, 13].

Although PCs are common concrete admixtures, the behavior of PC-based superplasticizers in cementitious systems is complex and the adsorption properties are still not well understood [16, 21, 43, 56]. However, PCs are designed so that the backbone adsorbs onto the various phases of cement and hydrates (most containing calcium) and the PEO “teeth” remain in pore solution. Researchers have found that the carboxylic group preferentially binds to the Ca^{2+} sites [44, 51, 52]. Similar adsorption behavior is expected on the nano CaCO_3 . However, it may be possible to improve dispersion by trying different architectures of the superplasticizer. The chemical structure of PC-based superplasticizers can be varied by changing its side chain length and density, which will effectively change its anionic charge density. These parameters can have a significant effect on their adsorption and dispersing capabilities [12, 31, 33, 53, 55]. Since commercially available superplasticizers like the one used in the present study are designed to disperse cement particles and hydrates, their architecture is likely not the most suitable for nano CaCO_3 . It is necessary to synthesize the PCs and systematically vary chain lengths and densities to determine what is most suitable for nano CaCO_3 . This was not within the scope of the present study but could be the topic of future work.

3.1.3 SEM imaging

As measured through absorbance spectra, results show that nanoparticles treated with PC and subjected to sonication lead to improved dispersion. To complement these results, suspensions prepared by mechanical stirring, HS and bath sonication are observed under SEM. Since the samples need to be dried for SEM imaging, it does not capture their true state in suspension. Despite this limitation, it can still provide information on the state of aggregation for comparative purposes.

The results are shown in Fig. 5. It is apparent that nanoparticles that are stirred still remain highly aggregated, Fig. 5a, with aggregates exceeding 20 μ .

This is similar to the state of the nanoparticles in the dry powder form, Fig. 1. On the other hand, with sonication the particles are in a plane and no large aggregates are present, as shown in Fig. 5b. This supports that the method is aiding the dispersion process by breaking up aggregates.

3.2 Early-age properties

The sedimentation that occurs over a long term is not ideal. However, for the purposes of evaluating the influence of dispersed nano CaCO_3 on the properties of fly-ash cementitious materials, the level of dispersion at the time of sample preparation is the most critical. It is possible to cast cementitious samples for mechanical testing within 1 h after sonication. Therefore the degree of dispersion over 1 h is important. According to Fig. 4, at least 85 % is retained after 1 h and 70 % after 3 h for all samples. It can thereby be assumed that

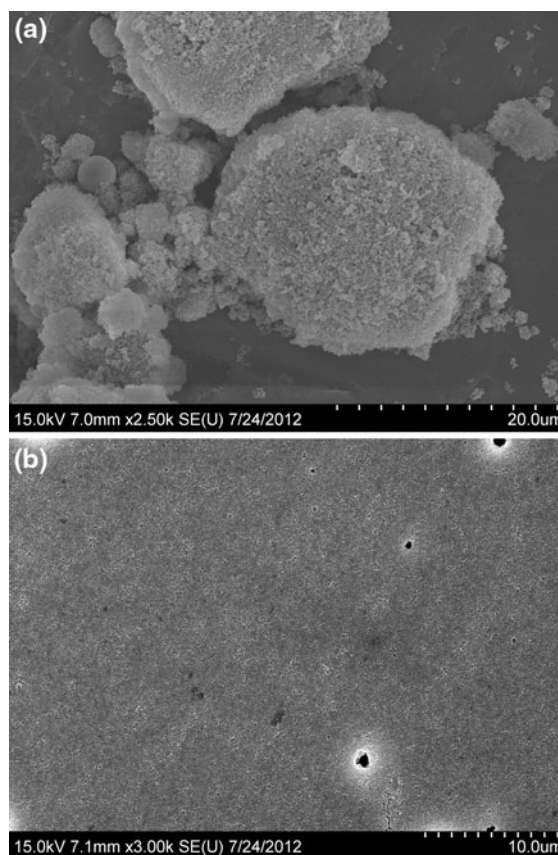


Fig. 5 SEM images of nano CaCO_3 particles treated with PC (0.33 % by mass) and prepared by **a** mechanical stirring and **b** bath sonication [27]

if the samples are cast within this time frame, the majority of the nanoparticles are still dispersed and suspended. Additionally, the nanoparticles can be sonicated again to re-disperse in solution moments before sample preparation, which enhances the economic viability of such a product.

3.2.1 Setting

The setting times of CPs with 30 % fly ash replacement are compared against that of plain CP. 30 % fly ash-CPs without nanoCaCO₃ (30FA) and with 1 % nanoCaCO₃ (1nLS) dispersed either by stirring or ultrasonication are compared. For both dispersion methods, the nanoparticles are treated with PC, added at a concentration of 33 % by mass of nanoCaCO₃. All samples (including those without any nanoparticles) have a 0.33 % PC addition by mass of binder.

The results are shown in Fig. 6. Two samples are tested for each mix. The replacement of 30 % of cement with fly ash delays initial and final set by approximately 2 h. With the addition of 1 % nanoCaCO₃ in both cases, stirred and sonicated, setting is accelerated. With the stirred nanoparticles, initial and final set are shortened by approximately 1 h. There is greater improvement with the sonicated nanoparticles, where set time is accelerated by more than 1.5 h. This indicates that sonication enhances the effect of the nanoparticles. This is likely due to the seeding effect, which increases with improved dispersion. Well-dispersed nanoparticles can accelerate the start of the

main hydration phase and increase the number of nucleation sites from which C–S–H can grow. The latter allows the microstructure to become percolated more rapidly and subsequently lead to faster setting. There may also be a filler effect, where the nanoparticles are providing more contact points within the structure, therefore leading to an interconnected network more rapidly.

3.2.2 Compressive strength gain

The compressive strengths at 1, 3 and 7 days are compared for 30 % fly ash-CPs with PC-treated, sonicated nanoCaCO₃. Mixes with nanoCaCO₃ additions of 1, 2.5 and 5 % (1nLS, 2.5nLS, and 5nLS) by mass of binder are compared. The mix designs are shown in Table 6. In mixes 2.5nLS and 5nLS, the PC concentration is 16.5 and 8.3 % by mass of nanoCaCO₃, respectively. (This corresponds to 0.4 % by mass of binder for both cases.) According to the results of the dispersion tests, see Table 5, a PC concentration of 16.5 % still returns sufficient dispersion while at 7 % the degree of dispersion goes down significantly. However, the addition of PC allowable is limited by the rheological properties of the CPs, where increasing the PC addition in the pastes any more than 0.4 % would lead to segregation and bleeding. At 1 % nanoCaCO₃ addition the suspensions are horn sonicated for 3 h at 40 % amplitude while at 2.5 and 5 % the suspensions are bath sonicated for 9 h.

In Fig. 7, the influence of 30 % fly ash replacement and 1 % nanoCaCO₃ are shown. The replacement of 30 % of cement with fly ash leads to a decrease in strength gain at all ages compared to the plain CP. With the addition of 1 % nanoCaCO₃, there is little influence at 1 and 3 days, as shown in the strengths for both mixes 1nLS (sonicated) and 1nLS (stirred). However, by

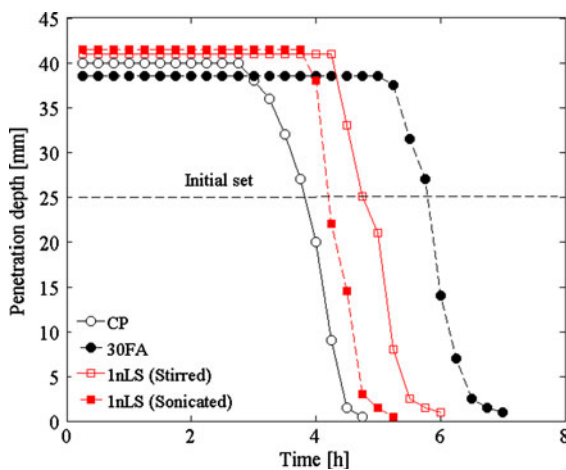


Fig. 6 Setting time: plain cement paste (CP) and 30 % fly ash-cement pastes with 0 % (30FA) and 1 % nanoCaCO₃ (1nLS) addition [27]

Table 6 Mix design for compressive strength paste samples

| Mix | Cement (g) | Fly ash (g) | Water (g) | NanoCaCO ₃ (g) | PC (g) |
|--------|------------|-------------|-----------|---------------------------|--------|
| CP | 750 | 0 | 262.5 | 0 | 2.5 |
| 30FA | 525 | 225 | 262.5 | 0 | 2.5 |
| 1nLS | 525 | 225 | 262.5 | 7.5 | 2.5 |
| 2.5nLS | 525 | 225 | 262.5 | 18.8 | 3.1 |
| 5nLS | 525 | 225 | 262.5 | 37.5 | 3.1 |

Water, nanoCaCO₃, and PC added as suspension prepared by bath sonication

7 days the sonicated mix exhibits higher strength than the plain 30FA sample by approximately 15 %. The stirred mix, on the other hand, exhibits a slightly lower strength than 30FA. This may be attributed to aggregation. Due to the high surface energy of the nanoparticles, the aggregates have the capacity to entrain air. As a result, the aggregates will act as weak points in the material and result in stress concentration. Similar to what is seen in the setting time results, sonication and PC treatment enhances the effect of the nanoparticles by improving dispersion. The exact mechanisms for the increase in strength at 7 days by the nanoCaCO₃ is unknown but can be the topic of future work.

The effect of higher additions of nanoCaCO₃ is determined and shown in Fig. 8. It is apparent that the most improvement is achieved with a 2.5 % nanoC-aCO₃ addition, with a 20 % increase in strength for 2.5nLS at 7 days compared to 30FA. It is likely that the improvement in mechanical properties exhibited by mixes 1nLS and 2.5nLS are due to seeding and filler effects. It should be noted that the PC dosage is not constant throughout all mixes and this can affect strength results, with higher PC potentially leading to lower strength due to increased susceptibility to segregation and void formation. However, 2.5nLS exhibits the highest strength despite having a higher PC content. And 2.5nLS and 5nLS can be compared directly as they have the same PC content.

With the addition of 5 % nanoCaCO₃, the improvement in strength gain is less significant at 7 days and even detrimental at 1 day. Again, this can be tied to issues of dispersion. First, this is a relatively high

concentration of nanoparticles. Dispersion becomes increasingly more difficult as the concentration increases—due to the proximity of the particles they are more likely to reaggregate. Second, the PC concentration is limited to 8.3 % by mass of nanoC-aCO₃ because a higher dosage would lead to segregation and bleeding of the CP. Dispersion results showed that the surface treatment is not sufficient at this concentration.

3.2.3 SEM

To better understand the compressive strength development of the various mixes and to complement the quantitative measure of dispersion obtained through spectroscopy, the morphology of 7 day pastes are examined through SEM. At least 15 images are captured at random locations on each sample. SEM images of plain CP and 30 % fly ash—CPs with 2.5 and 5 % nanoCaCO₃ addition are presented in Fig. 9.

The plain CP has an apparently compact microstructure filled with hydration products, shown in Fig. 9a, where an abundance of fibrillar C–S–H and CH can be seen. Compared to the plain CP, there are no marked differences in morphology in the 30 % fly ash—CP with 2.5 and 5 % nanoCaCO₃ addition (Fig. 9b, c, respectively), as can be resolved from SEM imaging. However, the compressive strength of the 2.5nLS samples at 7 days is notably greater than that of the 5nLS samples. Based on the SEM imaging technique utilized, no conclusions can be made on the effect of nanoCaCO₃ in altering the microstructure.

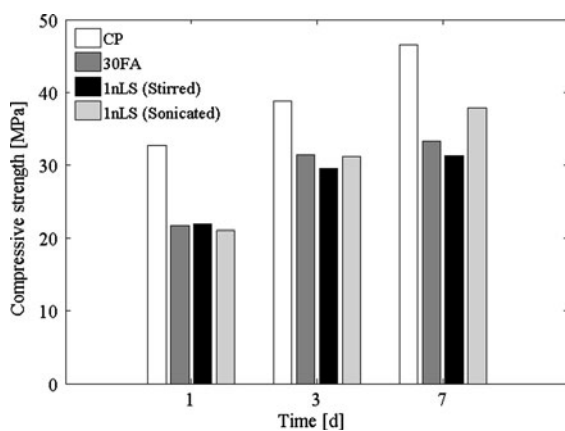


Fig. 7 Compressive strength gain: plain cement paste (CP) and 30 % fly ash—cement pastes with 0 % (30FA) and 1 % nanoCaCO₃ (1nLS) addition [27]

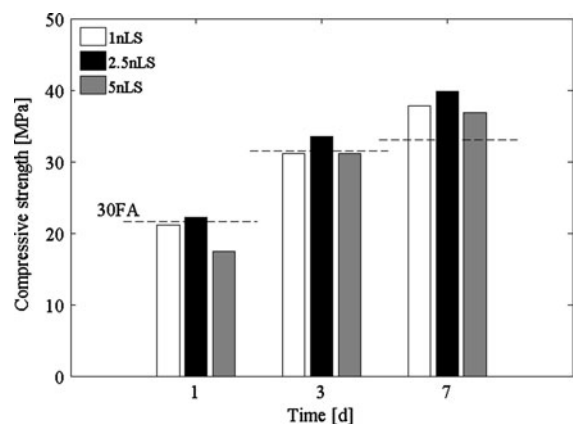


Fig. 8 Compressive strength gain of 30 % fly ash—cement pastes with 1, 2.5, and 5 % nanoCaCO₃ addition compared against 30 % fly ash—cement paste (30FA) [27]

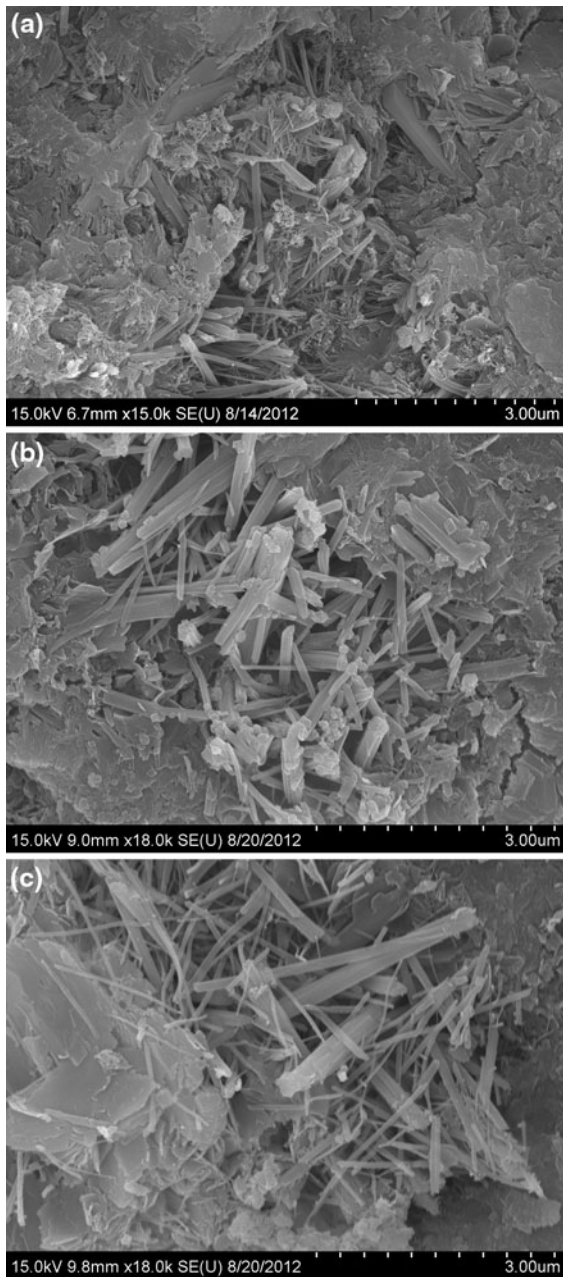


Fig. 9 SEM images of **a** plain cement paste and 30 % fly ash-cement pastes with **b** 2.5 % and **c** 5 % nanoCaCO₃ additions (Age = 7 days) [27]

But the strength behavior can be at least partially explained by the difference in degree of aggregation that occurs in each of the two mixes.

A higher degree of aggregation occurs in the fly ash-CP with 5 % nanoCaCO₃, where a number of aggregates are spotted during SEM imaging, shown in

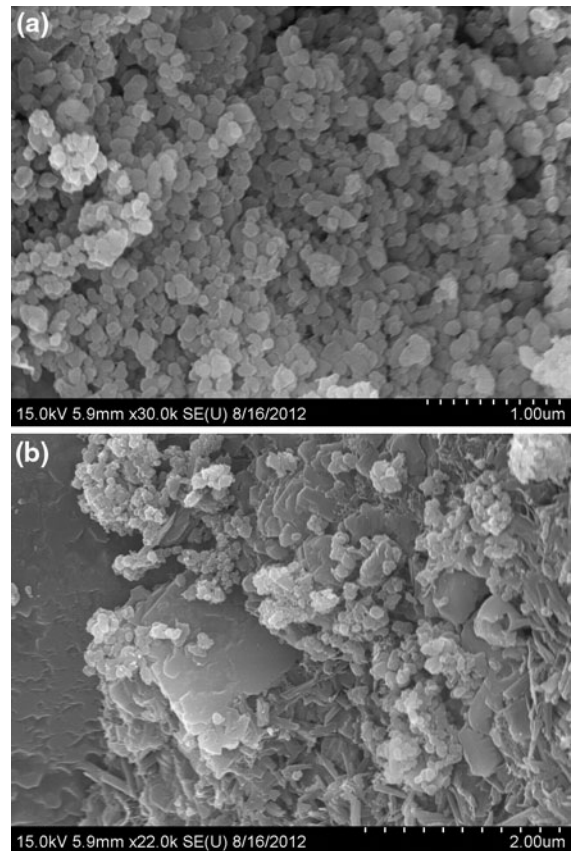


Fig. 10 SEM images of nanoCaCO₃ aggregates in 5 % nanoCaCO₃ fly ash-cement paste (Age = 7 days) at **a** 30 k and **b** 22 k magnification [27]

Fig. 10. Visually, they are similar to the SEM images of the nanoCaCO₃ from an aqueous solution, Fig. 5. EDS analysis also supports that they are CaCO₃, as they exhibit C/Ca ratios of about 0.7. In comparison, hydrates exhibit either very low traces of carbon or none at all. Therefore, SEM images support that although the nanoCaCO₃ is aiding in densifying the microstructure in both systems, the lower compressive strength exhibited by the 5nLS samples may be attributed to the higher degree of aggregation. It also confirms that aggregated nanoparticles do not contribute to seeding; otherwise they would not be visible in the microstructure at 7 days.

4 Conclusions

In this study there was a focus on quantitatively measuring the dispersion of CaCO₃ nanoparticles and tying it to their influence on the early-age properties of

fly ash-CPs. From the surfactants studied, polycarboxylate superplasticizer is found to be the most effective at dispersing the nanoCaCO₃ in aqueous solution. It may be possible to further enhance its adsorption and dispersion capabilities by altering the polymer's architecture, which would improve the practical viability of the approach. Results indicate that sonication aids in the dispersion process by physically breaking up the nanoparticles. However, there appears to be a limit to the extent to which modifying the amplitude and duration can further improve dispersion and stability. With sonication and treatment with PC, nanoCaCO₃ is found to accelerate setting and improve 7 days strength gain of fly ash-CPs, as compared to stirred samples. At 2.5 % addition, nanoCaCO₃ improves strength by 20 % at 7 days. At 5 % addition, there is a slightly negative effect due to aggregation, as indicated by the results of dispersion tests and SEM imaging.

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